

A phenomenological model for positronium formation at critical micelle concentration

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Abstract A diffusion-recombination model for positronium formation in aqueous solutions of surfactants is shown to reproduce correctly the general features of the dependence of positronium formation on critical micelle concentration

Keywords Positronium, micelle, surfactants

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1. Introduction

A rather dramatic decrease in the intensity (I_{ortho}) of the orthopositronium component of positronium (Ps) has been found to occur at the critical micelle concentration (CMC) for aqueous solutions of various surfactants in several experimental studies [1-5]. The objective of this paper is to show that the systematics for the decrease in I_{ortho} with increasing CMC (for different surfactants) is well described by a model proposed by Byakov and Stepanov [6].

2. Model

The energetic positrons emitted by a radioactive source on entering water dissipate their energy through ionization producing several bunches of ion-electron pairs called spurs [7]. Near the end of their tracks the slowed down positrons enter a diffusive regime where so-called blobs are formed each consisting of a positron with several ion-electron pairs distributed around it with near spherical symmetry. If the number of acts of ionization is N and the spur size is a_{spur} , then the radius of the blob may be estimated to be $a = N^{1/3} a_{spur}$. The electrons, ions and the positron participate in the processes of diffusion and recombination inside this blob. The main recombination channels in water are :

- a) Electron solvation : $e^- \rightarrow e_s^-$, with a rate constant $1/\tau_{es}$ (where τ_{es} is the solvation time), through which the electrons are caged by the polar water molecules and become inaccessible to the positron and thus unavailable for positronium formation.

- b) Ion-molecular reaction : $H_2O^+ + H_2O \rightarrow H_3O^+ + OH$, with a rate constant τ_{imn}^{-1} , due to which the H_2O^+ ions are scavenged by the water molecules.
- c) Ion (or hole)-electron recombination : $e^- + H_2O^+ \rightarrow H_2O^*$ with a rate constant K_{eh} followed by reactions into neutral species (H_2O , $H_2 + O$, $H + OH$) whereby the H_2O^+ ion, acting as a scavenger for the electron, is removed from the scenario.
- d) Positronium (Ps) formation : $e^+ + e^- \rightarrow Ps$ with a rate constant K_{ep} through which the positron, at the terminal end of its track, combines with a quasi-free electron to form the positronium.

When the surfactant is added to water at and above a certain critical concentration (CMC) aggregated structures (known as the micelles) are formed, which could be positively or negatively charged. Positively charged micelles act as effective acceptors for electrons with a capture rate constant K_{cm} , while negatively charged micelles act as acceptors for positrons and H_2O^+ ions with corresponding capture rate constants K_{pm} and K_{hm} respectively. Non-ionic micelles on the other hand could capture all these charged species (e^+ , e^- , H_2O^+). The basic cause for the drastic decrease in Ps formation at surfactant concentrations above CMC resides in the presence of micelles in the solution forcing the segregation of the position and the knocked out electrons.

3. Results and discussions

Incorporating diffusion into the recombination scheme outlined above leads to the following coupled differential equations for the concentrations (C_i) of different species written in a generic form to include micelles of different charges

$$\frac{\partial C_e}{\partial t} = D_e \nabla^2 C_e - K_{eh} C_e C_h - K_{ep} C_e C_p - \frac{C_e}{\tau_{imn}} - K_{em} C_e C_M \quad (1)$$

$$\frac{\partial C_h}{\partial t} = D_h \nabla^2 C_h - K_{eh} C_e C_h - \frac{C_h}{\tau_{imn}} - K_{hm} C_h C_M \quad (2)$$

$$\frac{\partial C_p}{\partial t} = D_p \nabla^2 C_p - K_{ep} C_e C_p - K_{pm} C_p C_M, \quad (3)$$

where D_e , D_h and D_p are the diffusion coefficients for electrons, H_2O^+ (holes) and positrons respectively. The concentrations $C_i(r, t)$ are functions of space and time where r is measured from the centre of the blob and t from the instant of entry into diffusion regime. The micellar concentration C_M is held fixed as they merely act as sinks for e , h , p as the case may be. It is convenient to separate out the effect of diffusion from that of recombination by writing $C_i(r, t) = n_i(t) W_i(r, t)$ where $W_i(r, t)$ is simply the solution of the diffusion equation, which assuming ambipolar diffusion, forced by the requirement of charge neutrality in dilute solutions, whereby $D_e \sim D_p \sim D_h \equiv D$ yields

$$W_e \sim W_n \sim W_h \equiv W = \frac{1}{[\pi(4Dt + a^2)]^{3/2}} \exp \quad (4Dt + a^2) \quad (4)$$

where a is the radius of the blob introduced earlier. Here W is normalized to unity, namely, $\int W_i(\mathbf{r}, t) d^3\mathbf{r} = 1$. Through this device the equations for the concentrations C_i may be translated into equations for the survival number densities (n_i). The influence of the lone positron in the blob on n_e and n_h can be justifiably neglected. It is also convenient to introduce $\tau_e^{-1} = \tau_{es}^{-1} + K_{em}C_M$, $\tau_h^{-1} = \tau_{hr}^{-1} + K_{hm}C_M$, $\tau_p^{-1} = K_{pm}C_M$. The equations for n_i should be solved with the initial condition $n_e(t=0) = n_h(t=0) = n_e$ (the number of ion-electron pairs in the blob) and $n_p(t=0) = 1$. Byakov and Stepanov make the approximation $\tau_p^{-1} = 0$ and $\tau_{es} / \tau_{hr} \ll 1$ which is really not quite tenable, but we can obtain a solution relaxing these approximations.

The probability for positronium formation is given by the product of the concentration $C_e(\mathbf{r}, t)$ and $C_p(\mathbf{r}, t)$ for the electron and the positron at a given point \mathbf{r} and at time t multiplied by the rate constant for positronium formation integrated over the diffusion region (blob) and over all time, namely,

$$P_{Ps} = \int_0^\infty dt \int d^3\mathbf{r} K_{ep} C_e(\mathbf{r}, t) C_p(\mathbf{r}, t) \quad (5)$$

wherein, inserting our solution to the rate equations results in

$$P_{Ps} = \frac{K_{ep}}{K_{eh}} \int_0^\infty d\xi \frac{\psi(\xi, \tau / \tau_e) \exp(-\xi \tau / \tau_p)}{\left[1 + \int_0^\xi \psi(\xi', \tau / \tau_e) d\xi' \right]^{1+K_{ep}/K_{eh}}} \quad (6)$$

where $\psi(\xi, \tau / \tau_e) = \frac{\tau}{\tau_{hr}} \frac{\exp(-\xi \tau / \tau_p)}{(1+\xi)^{3/2}}$ and $\tau_{hr}^{-1} = \frac{K_{eh}n_0}{(2\pi a^2)^{3/2}}$ and $\tau = \frac{a^2}{4D}$ is the characteristic diffusion time to cover the blob expanse a . From this expression for P_{Ps} , one may estimate I_{ortho} which is $\frac{3}{4} P_{Ps}$. However, this requires values for the rate constants and diffusion coefficients.

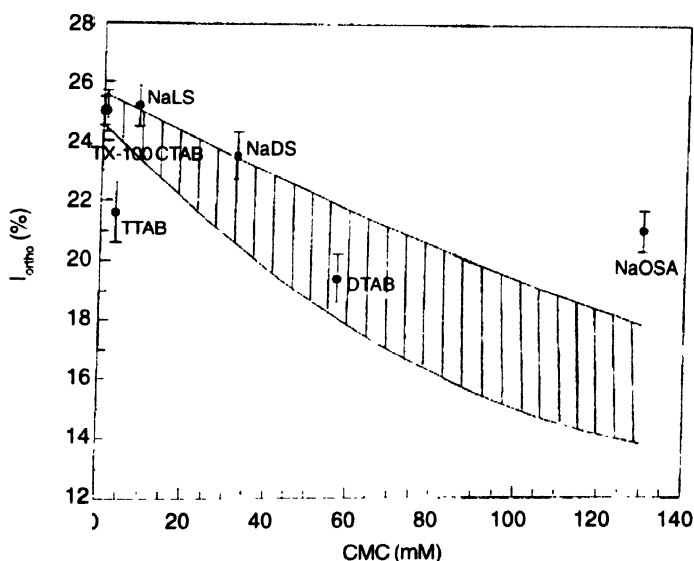


Figure 1. Ortho-positronium intensity vs CMC in aqueous surfactant solution. The shaded area included between the solid lines designates the theoretical band for I_{ortho} . The experimental data pertains to the surfactants in order of increasing CMC

A crucial parameter is the ratio of rate constants $\frac{K_{rp}}{K_{rh}}$ which Byakov and Stepanov have taken it to be ~ 1 based on a diffusion limited rate constant. We, on the other hand, incorporate the energy dependence of the rate constants (by augmenting the reaction radii due to the de Broglie wavelengths of the participant in a semi-classical spirit) and arrive at a value of ~ 2 for this ratio. The uncertainties in the main parameters of the model may be taken into account by considering a range of values for the diffusion coefficient D around a central value of $1/3$, as also for the ratio $\frac{K_{rp}}{K_{rh}}$ of rate constants and the spread in energy value of the positron at the end of the track. Since our emphasis is to see the effect of the surfactants in the neighbourhood of CMC, we have pinned down the probabilities of positronium formation in water to its experimental value. Accordingly, we have used the value $\tau_{es} = 0.3 \times 10^{-12}$ sec. and $\tau_{es} / \tau_{ter} = 0.28$. From radiolytic data we have adopted the assignments $N = 10$, $a_{spur} = 70 \times 10^{-8}$ cm and $n = 100$. The theoretical uncertainties have resulted in a band for $I_{ortho}(\%)$ which is shown in Figure 1 as a shaded region together with the experimental points for different surfactants with error bars.

4. Conclusions

The diffusion recombination model of Byakov and Stepanov could be successfully used to delineate the dependence of positronium formation intensity ($I_s\%$) of the micellar solutions as a function of their respective CMCs. Except for one, (*ie.* Sodium octyl sulphate, NaOSA, in water) with a high CMC value of 130 mM, all the other experimental data available to us lie in the theoretically predicted region within a standard deviation.

One of the important limitation of the model, in this case is due to the simplified assumptions of ambipolar diffusion at sufficiently dilute and low ionic strength of the solution, which fails to work at high surfactant concentrations.

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